

SEPARABILITY OF COLD LAKE BITUMEN AND ARABIAN HEAVY VACUUM RESID

Irwin A. Wiehe*
Soluble Solutions
3 Louise Lane
Gladstone, NJ 07934

KEYWORDS: heavy oil, separability, molecular limits

INTRODUCTION

While refinery separation of heavy oil is usually restricted to distillation, fluid catalytic cracking (FCC) feed is not required to be volatile, only containing acceptable levels of catalyst poisons: Conradson carbon residue, vanadium, nickel, and basic nitrogen. One method for achieving this objective is to physically separate the higher quality fraction. Therefore, the laboratory separation of Cold Lake bitumen and Arabian Heavy vacuum resid was done to determine the potential for a more molecularly selective separation. The combination of distillation, deasphalting, and adsorption was used to determine the ultimate separation that is possible in order to approximate the molecular limits, or the molecular separability.

The feed specifications for fluid catalytic cracking of resid containing oils depend greatly on the design and practice of the FCC unit, on the catalyst, and on other feeds available for blending. Nevertheless, the typical guidelines of Barnes (1), shown in Table 1 will be used. Of these, Conradson carbon residue, vanadium content, and nickel content are often the most critical and will be emphasized.

Table 1
Feed Specifications for Resid FCC (1)

<u>Feed Property</u>	<u>Limit</u>
Conradson Carbon Residue	3 - 8 wt%
Vanadium Content	10 - 15 ppm
Nickel Content	20 - 25 ppm
Sodium Content	5 - 10 ppm
Basic Nitrogen	800 ppm
Sulfur Content	3 wt%
Maximum Density	0.940 g/cc
Minimum Hydrogen	11.5 wt%

EXPERIMENTAL

The general procedure used for separating heavy oils as shown in Figure 1 is a variation of that published previously (2). The first possible step was batch distillation at 1.4 mm Hg that was done directly out of tubing bombs immersed in a sand bath at 315° C. The second and third steps were repeated using several solvents but the same solvent for each step for a given trial. The second step removed the solvent insolubles by mixing 25 parts solvent to one part oil, waiting eight hours, and filtering. In the third step Attapulugus clay was mixed with the oil dissolved in the solvent and let sit for eight hours. This mixture was filtered with a fine glass frit and washed with additional solvent until the solvent passed through clear of any color. The heavy oil dissolved in the solvent was recovered by rotary evaporation and vacuum drying. The fraction remaining on the clay was recovered by washing on the glass frit with a mixture containing 50% acetone and 50% toluene followed with 10% methanol and 90% toluene. Finally, the adsorbed fraction of heavy oil was recovered from the solvents by rotary evaporation and vacuum drying. The solvents used in the separation trials included n-pentane, n-heptane, cyclohexane, toluene, and carbon disulfide. Once collected, analytical data were measured on each of these fractions.

RESULTS AND DISCUSSION

Separation of Heavy Oils

For the separation of each heavy oil, each quality measurement: Conradson carbon, vanadium, nickel, etc., in the higher quality fraction was plotted versus the yield of the higher quality fraction. Since the highest quality fraction was the distillable liquids, it was the point at the lowest yield for Cold Lake bitumen. The soluble, but unadsorbed, fraction was the next highest quality fraction for each trial solvent. Thus, the quality measurement and yield were calculated as if this fraction and the distillable liquids were mixed to form the second point for each trial

* Research was done at Exxon Corporate Research, Annandale, NJ 08801-0998

solvent. Likewise, the soluble adsorbed fraction and the insolubles were added. This type of data for Conradson carbon residue is shown in Figure 2 for Cold Lake bitumen and in Figure 3 for Arabian Heavy Vacuum resid. In each case a curve is drawn through those of highest yield at a given quality measurement as this determines the best way the heavy oil could be split into two fractions, the separability.

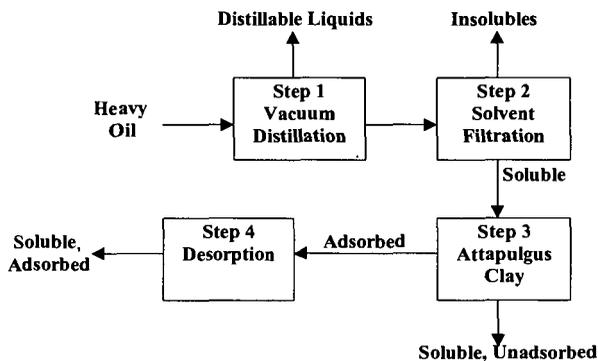


Figure 1. General Procedure for Laboratory Selective Separation

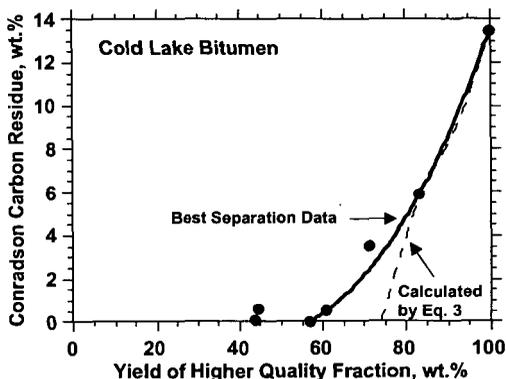


Figure 2. Selective Separation of Conradson Carbon for Cold Lake Bitumen

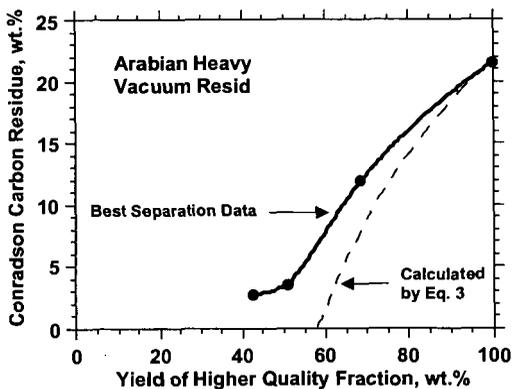


Figure 3. Selective Separation of Conradson Carbon for Arabian Heavy Vacuum Resid

Of the solvents tried, cyclohexane is the best because it gives a high yield of a high quality fraction without insolubles. The yields and analytical data for the cyclohexane separations are shown in Table II and compared with the starting feed data. Thus, for Arabian Heavy vacuum resid that does not require distillation, the separation is achieved in two steps, adsorption and desorption, and about half of the resid would meet the specifications for resid FCC feed in Table I except for sulfur. On the other hand, combining vacuum distillation with cyclohexane adsorption separates 71% of Cold Lake bitumen into a fraction that only slightly misses the example specifications for sulfur and hydrogen.

Table II
Cyclohexane Separations: Yields and Analytical Data

Fraction	Yield wt.%	C wt.%	H wt.%	N wt.%	O wt.%	S wt.%	V ppm	Ni ppm	Conradson
									Carbon wt.%
Cold Lake Bitumen									
Distillable Liquids	44.5	85.14	11.67	0.09	0.00	2.63	0.6	0.0	0.57
Soluble, Unadsorbed	26.7	84.08	10.96	0.17	0.60	4.11	29	10	8.4
<i>Dist. Liq. + Sol.</i>	<i>71.2</i>	<i>84.74</i>	<i>11.40</i>	<i>0.12</i>	<i>0.22</i>	<i>3.18</i>	<i>11</i>	<i>4</i>	<i>3.5</i>
<i>Unadsorb.</i>									
Soluble, Adsorbed	30.2	81.07	8.73	0.99	2.39	6.55	359	138	43.8
TOTAL	101.4	83.57	10.60	0.38	0.87	4.19	115	41	15.5
Full Feed	100	83.82	10.46	0.38	0.68	4.57	152	62	13.5
Arabian Heavy Vacuum Resid									
Soluble, Unadsorbed	50.9	85.07	11.47	0.030	0.50	3.57	0.0	0.0	3.4
Soluble, Adsorbed	50.1	82.63	8.53	0.80	1.63	6.78	451	112	36.9
TOTAL	101.0	83.86	10.01	0.41	1.06	5.16	224	56	20.2
Full Feed	100	83.51	9.93	0.45	0.57	5.80	165	40	21.5

Conradson Carbon Separability Limit

Here we will focus on the problem of maximizing the yield of a low Conradson Carbon fraction. 100 parts of heavy oil of C_F Conradson carbon is separated into β parts of a higher quality fraction containing a Conradson carbon of C_H and $100-\beta$ parts of a lower quality fraction containing a Conradson carbon of C_L . Since Conradson carbon is conserved for separations (3):

$$100 C_F = \beta C_H + (100 - \beta) C_L \quad [1]$$

Solving for β :

$$\beta = 100 [1 - (C_F - C_H) / (C_L - C_H)] \quad [2]$$

This shows that to maximize the yield of a high quality fraction meeting a Conradson carbon specification from a given heavy oil feed, one needs to concentrate the Conradson carbon in the low quality fraction. Therefore, for Cold Lake bitumen (Conradson carbon = 13.5 wt.%) to separate 85 wt.% of a fraction meeting a specifications of 5 wt.% Conradson carbon, one would need to isolate 15 wt.% containing 61.7 wt.% Conradson carbon. However, the highest Conradson carbon fraction that was isolated from Cold Lake bitumen is the 14.1 wt.% yield of n-heptane insoluble asphaltenes with a Conradson carbon of 52.5%. Thus, it is unlikely that 85 wt.% of a fraction of Cold Lake bitumen with a Conradson carbon of 5 wt.% or less exists because significant fractions of Conradson carbon much greater than 50 wt.% Conradson carbon are not present in heavy oils. This is because the coke precursors are chemically linked to distillable liquid precursors in the same molecule. In terms of the pendant - core building block model (3), all molecules that contain cores also contain significant fractions of pendants. For instance, Arabian heavy vacuum resid with a Conradson carbon of 21.5 wt.% and an asphaltene Conradson carbon of 51.6 wt.% at a specification of 5 wt.% Conradson carbon:

$$\beta = 100 [1 - (21.5 - 5) / (51.6 - 5)]$$

$$\beta = 64 \text{ wt.}\%$$

Thus, the separation of 64 wt.% of Arabian Heavy vacuum resid with a Conradson carbon of 5 wt.% or less is not possible because there are only 20 wt.% asphaltenes and not the 36 wt.% required. As a result, Eq. 2 with the asphaltene Conradson carbon substituted for C_L is an upper limit on the yield of a fraction of a given Conradson carbon value. Eq. 1 can be rearranged and the asphaltene Conradson carbon, C_A , substituted for C_L to give:

$$C_H = \{C_F - (1 - \beta/100) C_A\} / \{\beta/100\}$$

[3]

This upper limit, Eq. 3, is plotted on Figures 2 and 3 as a dashed curve. The curve through the best separation data approaches the upper limit at high yields of the higher quality fraction for Cold Lake bitumen. On the other hand, a gap remains between the two curves for Arabian Heavy vacuum resid, indicating further improvements in separability of this heavy oil may be possible.

Separation of Vanadium and Nickel from Heavy Oils

Unlike for Conradson carbon, the separability of vanadium and nickel is not limited much by the heavy oil macromolecules. Vanadium with an atomic weight of 50.9, even as part of the largest macromolecules, the asphaltenes of average molecular weight of 3000, would be 1/60 the weight of the molecule bonded to it. Thus, in Cold Lake bitumen that contains 152 ppm vanadium and Arabian Heavy vacuum resid that contains 165 ppm vanadium, all of the vanadium is in less than 1 wt.% of each heavy oil. Likewise, nickel at 62 ppm in Cold Lake bitumen and 56 ppm in Arabian Heavy vacuum resid must be contained in less than 0.5 wt.% of each heavy oil. Nevertheless, the vanadium and nickel containing molecules physically associate with the Conradson carbon precursors, the polynuclear aromatics. As a result, they tend to separate together. Figure 4 and 6 demonstrates for Cold Lake bitumen and Figures 5 and 7 for Arabian Heavy vacuum resid that only a little more low vanadium and nickel fractions can be separated than low Conradson carbon fractions (Figures 2 and 3). Thus, precipitation and/or Attapulugus clay adsorption do not provide the desired selective separation for vanadium and nickel.

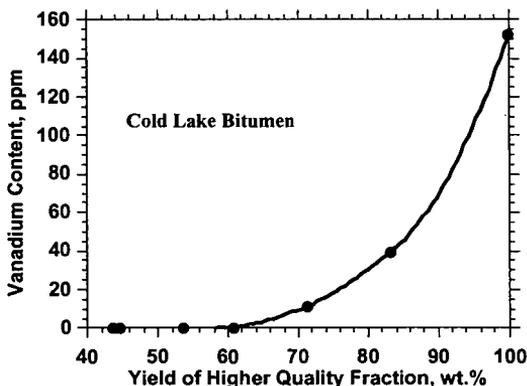


Figure 4. Selective Separation of Vanadium in Cold Lake Bitumen

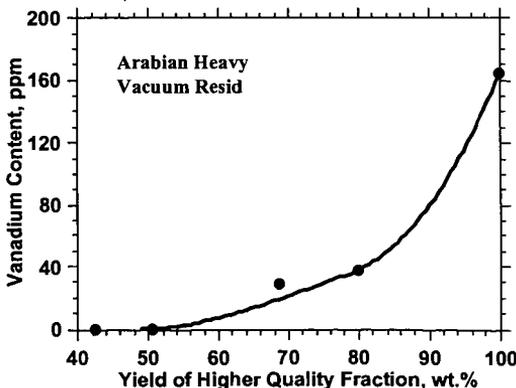


Figure 5. Selective Separation of Vanadium in Arabian Heavy Vacuum Resid

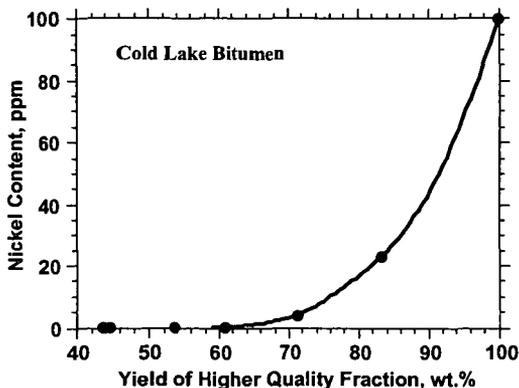


Figure 6. Selective Separation of Nickel in Cold Lake Bitumen

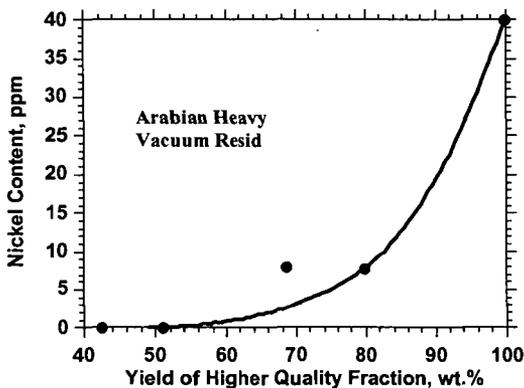


Figure 7. Selective Separation of Nickel in Arabian Heavy Vacuum Resid

CONCLUSIONS

Selective separation has the potential to provide substantial fluid catalytic cracking feed from heavy oils that could compete with resid conversion processes. Further separation of Conradson carbon is limited by heavy oil molecules in which Conradson carbon precursors are chemically bonded to significant fractions of distillable liquid precursors. On the other hand, there are no molecular limitations to the much greater separation of vanadium and nickel. Vanadium is in less than 1 wt.% of heavy oils and nickel is in less than 0.5 wt.%. Although sufficient for resid FCC specifications, physical association with Conradson carbon precursors tends to cause vanadium and nickel to separate with the Conradson carbon precursors in precipitation and adsorption separations. Thus, devising a molecularly selective separation method for attaining the full potential of metals removal from heavy oils remains to be a significant challenge.

REFERENCES

1. Barnes, P.H., AIChE, International Conference on Refinery Processes, Preprints, 1998, 227.
2. Wiche, I. A., *Ind. Eng. Chem. Res.* 1992, 31, 530.
3. Wiche, I. A., *Energy Fuels* 1994, 8, 536.